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⑬ Applicant: THE MEAD CORPORATION  
Mead World Headquarters Courthouse Plaza Northeast  
Dayton Ohio 45463 (US)

⑭ Inventor: Gottschalk, Peter  
71 Gershwin Drive  
Centerville Ohio 45459 (US)

Neckers, Douglas Carlyle  
108 Secor Woods  
Perrysburg Ohio 43551 (US)

Schuster, Gary Benjamin  
1911 Augusta Drive  
Champaign Illinois 61821 (US)

⑮ Representative: Bankes, Stephen C. D. et al  
Baron & Warren 18 South End Kensington  
London W8 5BU (GB)

⑯ Photosensitive materials containing ionic dye compounds as initiators.

⑰ A photohardenable composition comprising a free radical addition polymerizable or crosslinkable compound and an ionic dye-counter ion compound, said compound being capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization or crosslinking of said compound; and photosensitive material incorporating the same

EP 0 223 587 A1

## Description

## PHOTOSENSITIVE MATERIALS CONTAINING IONIC DYE COMPOUNDS AS INITIATORS

The present invention relates to novel photohardenable compositions and to photosensitive materials employing them. More particularly, it relates to free radical addition polymerizable compositions containing an ionic dye-counter ion complex such as a cationic dye-borate anion complex or an anionic dye-iodonium ion complex as a photoinitiator.

U.S. Patents 4,399,209 and 4,440,846 to The Mead Corporation describe imaging materials and imaging processes in which images are formed through exposure controlled release of an image-forming agent from a microcapsule containing a photohardenable composition. The imaging material is exposed image-wise to actinic radiation and subjected to a uniform rupturing force. Typically the image-forming agent is a color precursor which is released image-wise from microcapsules whereupon it reacts with a developer to form a visible image.

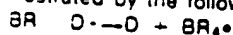
One of the problems which has been encountered in designing commercially acceptable panchromatic, full color imaging materials employing these techniques has been the relatively short wavelengths band to which most photohardenable compositions are sensitive to actinic radiation. In most cases, the compositions are only sensitive to ultraviolet radiation or blue light, e.g., 350 to 480 nm.

Full color photosensitive materials are described in U.S. Application Serial No. 339,917, filed January 18, 1982, and U.S. Application Serial No. 620,994 filed June 15, 1984. These imaging materials include a photosensitive layer which contains three sets of microcapsules. Each set of microcapsules is sensitive to a different band of radiation in the ultraviolet or blue spectrum and contains a cyan, magenta or yellow image-forming agent. The absorption spectra of the initiators employed in these microcapsules are never perfectly distinct. There is always some degree of overlap in the absorption curves and sometimes it is substantial. Exposure conditions therefore must be controlled carefully to avoid cross-exposure.

It would be desirable to extend the sensitivity of the photohardenable compositions used in these imaging materials to longer wavelengths. By extending the sensitivity of the photohardenable compositions to longer wavelengths, the amount of overlap in the absorption spectra of the initiators and the concomitant incidence of cross-exposure can be reduced. It would be particularly desirable if compositions could be designed with sensitivities to selected wavelength bands throughout the visible spectrum (400 to 700 nm) since this would provide a visible light-sensitive material which could be exposed by direct reflection or transmission imaging and without image processing.

It has been found that ionic dye-counter ion compounds, such as cationic dye-borate anion compounds, are useful photoinitiators of free radical addition reactions. Such compounds consist of a visible light absorber (the ionic dye) ionically bonded to a reactive counter ion. The counter ion is reactive in the sense that upon excitation of the dye the counter ion donates an electron to or accepts an electron from the excited dye. This electron transfer process generates radicals capable of initiating polymerization of a monomer.

The mechanism whereby the compounds absorb energy and generate free radicals is not entirely clear. It is believed that upon exposure to actinic radiation, the dye ion is excited to a singlet state in which it accepts an electron from or donates an electron to the counter ion. For a cationic dye-borate anion compound, this can be illustrated by the following equation:



The lifetime of the dye singlet state is extremely short by comparison to the lifetime of the triplet state. The quenching rate constants which have been observed suggest that the ionic compounds experience a very efficient electron transfer via the singlet state. In solution in the polymerizable compound, tight ionic pairing of the counter ion and the dye is believed to provide favorable spacial distribution promoting electron transfer to such an extent that the transfer occurs even though the lifetime of the singlet state is very short. Of course, this does not mean that electron transfer is restricted to the singlet state. Ionic dyes which have significant populations of triplet state may undergo electron transfer through the singlet state, triplet state, or both singlet and triplet states.

Upon transfer of the electron, a radical is formed. The ionic compounds used as initiators in the present invention do not appear to exhibit back electron transfer. It is believed that following electron transfer, the dye and counter ion become disassociated such that back electron transfer does not occur.

The ionic compounds used in the present invention are different than the collision generated species encountered in other photosensitive systems such as collision complexes which yield encounter complexes, exciplexes and/or contact ion pairs. See for example, Kavarnos, George J. and Turro, Nicholas J., "Photosensitization by Reversible Electron Transfer", *Chem. Rev.* 1986, 401-449.

In accordance with the present invention the ionic dye and the counter ion are present in the photopolymerizable composition as a stable, non-transient compound, and not as a dissociated ion pair. Formation of the compound is not dependent upon diffusion and collision. As distinguished from photographic materials and compositions containing collision dependent complexes essentially all of the sensitizing dye present in the photosensitive materials of the present invention prior to exposure is ionically bonded to the counter ion.

The ionic compounds used as initiators in the present invention can also be characterized in that they are soluble in nonpolar solvents such as TMPTA and the like. They are soluble in an amount of at least about 0.10%

and preferably at least about 0.39. While these amounts are not large, they are substantial considering the normally lower solubility of ionic materials in polar solvents. While the compounds are soluble, the dye and the counter ion do not dissociate in solution. They remain ionically bonded to each other.

In dye-sensitized photopolymerizable compositions, visible light is absorbed by a dye having a comparable absorption band, the dye is raised to its excited electronic state, the lifetime of which may be  $10^{-9}$  to  $10^{-8}$  second, depending upon the nature (singlet or triplet) of the excited state. During this time, absorbed energy in the form of an electron must be transferred to or from the dye molecule to produce the free radical. In prior initiator systems, this transfer is diffusion controlled. The excited dye must interact (collide) with another molecule in the composition which quenches the dye and generates a free radical. In the present invention, the transfer is not diffusion (collision) controlled. Electron transfer occurs at greater than diffusion controlled rates. In terms of Stern-Volmer kinetics, this means the quenching constant (Kq) of the excited dye is greater than  $10^{10}$  and, more particularly, greater than  $10^{12}$  have been observed for the ionic compounds. At these rates, electron transfer can occur through the singlet state.

Thus, the present invention provides a means for generating free radicals from the excited state of an ionic dye and insodoing provides photohardenable compositions which are sensitive at longer wavelengths.

One of the particular advantages of using ionic dye-counter ion compounds as initiators of free radical addition reactions is the ability to select from a wide variety of dyes which absorb at substantially different wavelengths. The absorption characteristics of the compound are principally determined by the dye. Thus, by selecting a dye which absorbs at 400 nm or greater, the sensitivity of the photosensitive material can be extended well into the visible range. Furthermore, compounds can be selected which are respectively sensitive to red, green and blue light without substantial cross-talk.

The ionic dye-counter ion compounds are particularly useful in providing full color photosensitive materials. In these materials, a layer including three sets of microcapsules having distinct sensitivity characteristics is provided on a support. Each set of microcapsules respectively contains a cyan, magenta, and yellow color-forming agent.

The absorption characteristics of the three sets of microcapsules in a full color photosensitive material must be sufficiently different that the cyan-forming capsules can be differentially hardened at a predetermined wavelength or over a predetermined wavelength range without hardening the magenta or yellow-forming capsules and, likewise, the magenta-forming and yellow-forming capsules can be selectively hardened upon exposure respectively to second and third wavelengths without hardening the cyan-forming capsules or hardening the other of the yellow-forming or magenta-forming capsules. Microcapsules, having this characteristic (i.e., cyan-, magenta- and yellow-forming capsules which can be selectively hardened by exposure at distinct wavelengths without cross-exposure) are referred to herein as having "distinctly different sensitivities."

As indicated above, because most photohardenable compositions are sensitive to ultraviolet radiation or blue light and they tend not to be sensitive to wavelengths greater than about 480 nm, it has been difficult to achieve microcapsules having distinct sensitivities at three wavelengths. Often it can only be achieved by carefully adjusting the exposure amounts so as not to cross-expose the capsules.

The present invention facilitates the achievement of distinct sensitivities by shifting the peak absorption of at least one of the initiators to higher wavelengths, such as wavelengths greater than about 400 nm. In this manner, instead of attempting to establish distinct sensitivities at three wavelengths within the narrow wavelength range of, for example, 350 nm to 480 nm, sensitivity can be established over a broader range of, for example, 350 to 550 nm or higher. In accordance with the invention, the sensitivity of the microcapsules can be extended well into the visible spectrum to 600 nm and in some cases to about 700 nm. In the preferred case compounds are provided which are respectively sensitive to red, green and blue light.

A principal object of the present invention is to provide photohardenable compositions which are sensitive to visible light, e.g., wavelengths greater than about 400 nm.

A further object of the present invention is to provide visible light-sensitive photohardenable compositions which are useful in the imaging materials described in U.S. Patents 4,399,209 and 4,440,846.

Another object of the present invention is to provide photohardenable compositions which are sensitive at greater than about 400 nm and which are useful as photoresists or in forming polymer images.

These and other objects are accomplished in accordance with the present invention which in one embodiment, provides:

A photohardenable composition comprising a free radical addition polymerizable or crosslinkable compound and a ionic dye-counter ion compound, said ionic dye-counter ion compound being capable of absorbing actinic radiation and producing free radicals which initiate free radical addition polymerization or crosslinking of said addition polymerizable or crosslinkable compound.

Another embodiment of the present invention resides in a photosensitive material comprising a support having a layer of photosensitive microcapsules on the surface thereof, said microcapsules containing an internal phase including a photohardenable composition comprising a free radical addition polymerizable or crosslinkable compound and a an ionic dye-counter ion compound.

Still another embodiment of the present invention resides in a photosensitive material useful in forming full color images comprising a support having a layer of photosensitive microcapsules on the surface thereof, said photosensitive microcapsules comprising a first set of microcapsules having a cyan image-forming agent associated therewith, a second set of microcapsules having a magenta image-forming agent associated

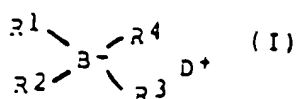
therewith, and a third set of microcapsules having a yellow image-forming agent associated therewith, at least one of said first, second, and third sets of microcapsules containing an internal phase which includes a photohardenable composition including a free radical addition polymerizable or crosslinkable compounds and an ionic dye-counter ion compound.

A further embodiment of the present invention resides in a photosensitive material comprising a support having a layer of a photohardenable composition on the surface thereof, said photohardenable composition comprising a free radical addition polymerizable or crosslinkable compound and an ionic dye-counter ion compound which provides a quenching constant (Kq) which is greater than  $10^{10}$  and preferably greater than  $10^{12}$ .

In accordance with more particular embodiments of the invention, the ionic compound is a cationic dye-borate anion compound and still more particularly a cyanine dye-borate anion compound; or an anionic dye compound such as ionic compounds of xanthene dyes with iodonium or pyrylium ions.

U.S. Patents 4,399,209 and 4,440,846 and U.S. Applications Serial No. 339,917, filed January 18, 1982, and Serial No. 620,994, filed June 15, 1984, are incorporated herein by reference to the extent that reference thereto may be necessary to complete this disclosure.

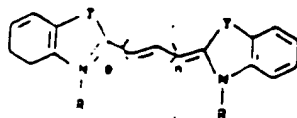
Cationic dye-borate anion compounds are known in the art. Their preparation and use in imaging systems is described in U.S. Patents 3,567,453; 4,307,182; 4,343,891; 4,447,521; and 4,450,227. The compounds used in the present invention can be represented by the general formula (I):



where D<sup>+</sup> is a cationic dye; and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from the group consisting of alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic and saturated or unsaturated heterocyclic groups.

Useful dyes form photoreducible but dark stable complexes with borate anions and can be cationic methine, polyethine, triarylmethane, indoline, thiazine, xanthene, oxazine, and acridine dyes. More specifically, the dyes may be cationic cyanine, carbocyanine, hemicyanine, rhodamine and azomethine dyes. In addition to being cationic, the dyes should not contain groups which would neutralize or desensitize the complex or render the complex poorly dark stable. Examples of groups which generally should not be present in the dye are acid groups such as free carboxylic or sulphonic acid groups.

Specific examples of useful cationic dyes are Methylene Blue, Safranin O, Malachite Green, cyanine dyes of the general formula (II) and rhodamine dyes of the formula (III):

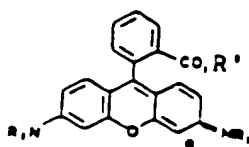


(II)

n = 0, 1, 2, 3,

R = alkyl

Y = CH=CH, N-CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>, O, S, Se



(III)

While they have not been tested, the cationic cyanine dyes disclosed in U.S. Patent 3,495,987 should be useful in the present invention.

The borate anion is designed such that the borate radical generated upon exposure to light and after

electron transfer to the dye (Eq. 1) readily dissociates with the formation of a radical as follows.  
 $BR_3 \rightarrow BR_2 + R^\bullet$  (Eq. 2)

For example particularly preferred anions are triphenylbutylborate and trianisylbutylborate anions because they readily dissociate to triphenylborane or trianisylborane and a butyl radical. On the other hand tetrabutylborate anion does not work well presumably because the tetrabutylborate radical is not stable and it readily accepts an electron back from the dye in a back electron transfer and does not dissociate efficiently. Likewise, tetraphenylborate anion is very poor because the phenyl radical is not easily formed.

Preferably, at least one but not more than three of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  is an alkyl group. Each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  can contain up to 20 carbon atoms, and they typically contain 1 to 7 carbon atoms. More preferably  $R^1$ - $R^4$  are a combination of alkyl group(s) and aryl group(s) or aralkyl group(s) and still more preferably a combination of three aryl groups and one alkyl group.

Representative examples of alkyl groups represented by  $R^1$ - $R^4$  are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, stearyl, etc. The alkyl groups may be substituted, for example, by one or more halogen, cyano, acyloxy, acyl, alkoxy or hydroxy groups.

Representative examples of aryl groups represented by  $R^1$ - $R^4$  include phenyl, naphthyl and substituted aryl groups such as anisyl. Alkaryl groups include methylphenyl, dimethylphenyl, etc. Representative examples of aralkyl groups represented by  $R^1$ - $R^4$  groups include benzyl. Representative alicyclic groups include cyclobutyl, cyclopentyl, and cyclohexyl groups. Examples of an alkynyl group are propynyl and ethynyl, and examples of alkenyl groups include a vinyl group.

As a general rule, useful ionic dye compounds must be identified empirically, however, potentially useful dye and counter ion combinations can be identified by reference to the Weller equation (Rehm, D. and Weller, A., *Isr. J. Chem.* (1970), 8, 259-271), which can be simplified as follows.

$$\Delta G = E_{ox} - E_{red} - E_{\gamma} \quad (\text{Eq. 3})$$

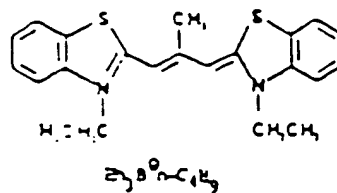
where  $G$  is the change in the Gibbs free energy,  $E_{ox}$  is the oxidation potential of the borate anion  $BR_3$ ,  $E_{red}$  is the reduction potential of the cationic dye, and  $E_{\gamma}$  is the energy of light used to excite the dye. Useful compounds will have a negative free energy change. Similarly, the difference between the reduction potential of the dye and the oxidation potential of the borate must be negative for the compounds to be dark stable, i.e.,  $E_{ox} - E_{red} > 0$ .

As indicated, Eq. 2 is a simplification and it does not absolutely predict whether a compound will be useful in the present invention or not. There are a number of other factors which will influence this determination. One such factor is the effect of the monomer on the complex. Another factor is the radial distance between the ions. It is also known that if the Weller equation produces too negative a value, deviations from the equation are possible. Furthermore, the Weller equation only predicts electron transfer, it does not predict whether a particular dye complex is an efficient initiator of polymerization. The equation is a useful first approximation.

Specific examples of cationic dye-borate anion compounds useful in the present invention are shown in the following table with their  $\lambda_{max}$ .

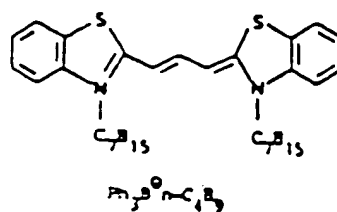
Compound No.Table  
Structure $\lambda_{\max}$  (TMPTA)

1.



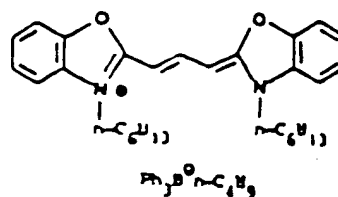
552 nm

2.



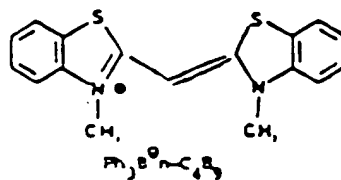
568 nm

3.



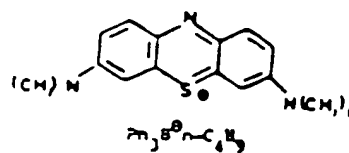
492 nm

4.



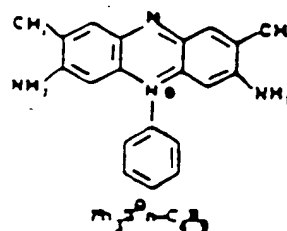
428 nm

5.



658 nm

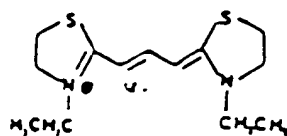
6.



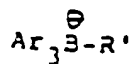
529 nm

0 223 587

7.



450nm



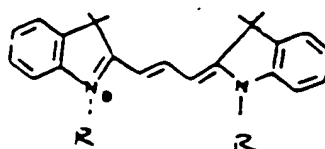
No.

R'

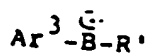
Ar

7A	n-butyl	phenyl
7B	n-hexyl	phenyl
7C	n-butyl	anisyl

3.



550nm



No.

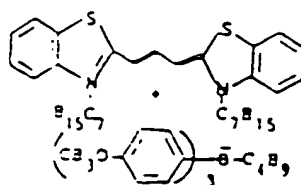
R'

R

Ar

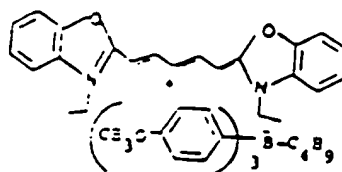
5A	methyl	n-butyl	phenyl
5B	methyl	n-hexyl	phenyl
5C	n-butyl	n-butyl	phenyl
5D	n-butyl	n-hexyl	phenyl
5E	n-heptyl	n-butyl	phenyl
5F	n-heptyl	n-hexyl	phenyl
5G	ethyl	n-butyl	phenyl

9.



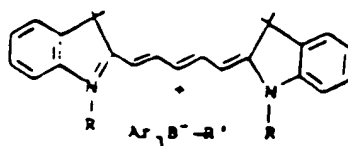
570 nm System

10.



590 nm System

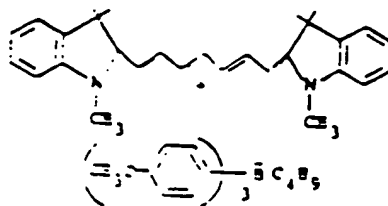
11.



640nm

No.	R	R'	Ar
11A	methyl	n-butyl	phenyl
11B	methyl	n-hexyl	phenyl
11C	n-butyl	n-butyl	phenyl
11D	n-butyl	n-hexyl	phenyl
11E	n-pentyl	n-butyl	phenyl
11F	n-pentyl	n-hexyl	phenyl
11G	n-heptyl	n-butyl	phenyl
11H	n-heptyl	n-hexyl	phenyl
11I	methyl	n-butyl	anisyl

12.



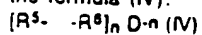
740 nm System

The cationic dye-borate anion compounds can be prepared by reacting a borate salt with a dye in a counterion exchange in a known manner. See Hishiki, Y., Repts. Sci. Research Inst. (1953), 29, pp 72-79.

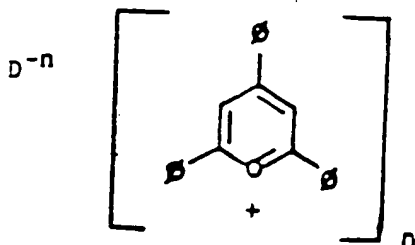


Useful borate salts are sodium salts such as sodium tetraphenylborate, sodium triphenylbutylborate, sodium trianisylbutylborate and ammonium salts such as tetraethylammonium tetraphenylborate.

Anionic dye compounds are also useful in the present invention. Anionic dye-iodonium ion compounds of the formula (IV):



where D- is an anionic dye and R<sup>5</sup> and R<sup>6</sup> are independently selected from the group consisting of aromatic nuclei such as phenyl or naphthyl and n is 1 or 2; and anionic dye-pyrylium compounds of the formula (V)



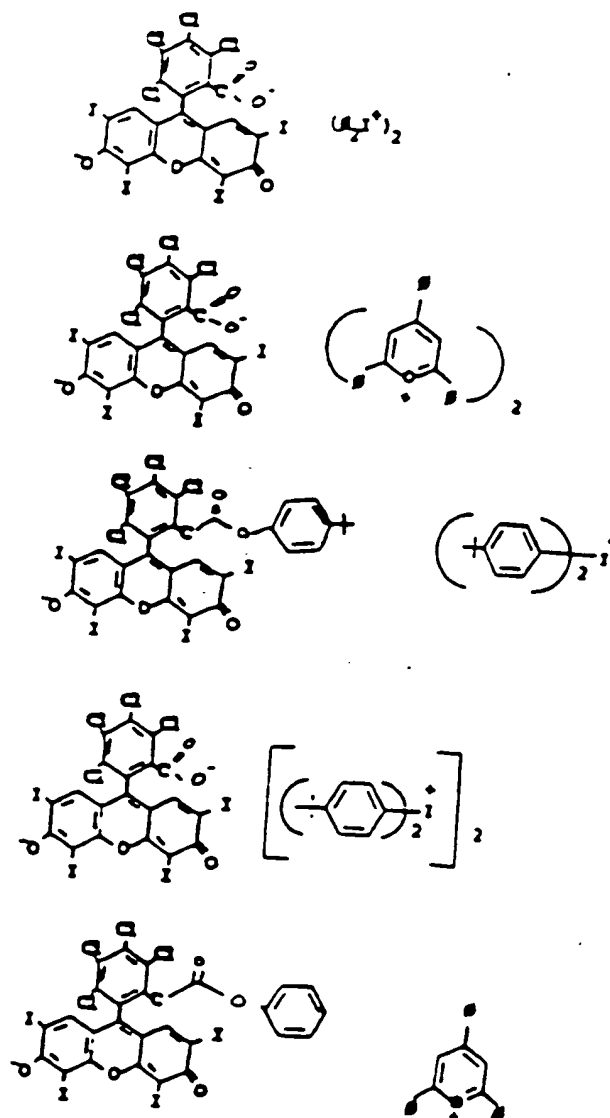
where D- and n are as defined above are typical examples of anionic dye complexes.

Representative examples of anionic dyes include xanthene and oxonols. In addition to iodonium and pyrylium ions, other compounds of anionic dyes and sulfonium cations are potentially useful.

As in the case of the cationic dye compounds, useful dye-cation combinations can be identified through the Weller equation as having a negative free energy.

Selected examples of anionic dye compounds are shown in Table 2 λ max. ca. 570 nm in TMPTA).

Table 2



The most typical examples of a free radical addition polymerizable or crosslinkable compound useful in the present invention is an ethylenically unsaturated compound and, more specifically, a polyethylenically

unsaturated compound. These compounds include both monomers having one or more ethylenically unsaturated groups, such as vinyl or allyl groups, and polymers having terminal or pendant ethylenic unsaturation. Such compounds are well known in the art and include acrylic and methacrylic esters of polyhydric alcohols such as trimethylolpropane, pentaerythritol and the like, and acrylate or methacrylate terminated epoxy resins, acrylate or methacrylate terminated polyesters, etc. Representative examples include ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylolpropane triacrylate (TMPTA), pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol hydroxypentacrylate (DPHPA), hexanediol-1,6-dimethacrylate, and diethyleneglycol dimethacrylate.

The ionic dye compound is usually used in an amount up to about 10% by weight based on the weight of the photopolymerizable or crosslinkable species in the photohardenable composition. More typically, the compound is used in an amount of about 0.2% to 0.5% by weight.

While the compound can be used alone as the initiator, film speeds tend to be quite low and oxygen inhibition is observed. It has been found that it is preferable to use the compound in combination with an autoxidizer. An autoxidizer is a compound which is capable of consuming oxygen in a free radical chain process.

Examples of useful autoxidizers are N,N-dialkylanilines. Examples of preferred N,N-dialkylanilines are dialkylanilines substituted in one or more of the ortho-, meta-, or para- position by the following groups: methyl, ethyl, isopropyl, t-butyl, 3,4-tetramethylene, phenyl, trifluoromethyl, acetyl, ethoxycarbonyl, carboxy, carbo-ylate, trimethylsilylmethyl, trimethylsilyl, methoxysilyl, trimethylgermyl, triethylgermyl, trimethylstannyl, n-butoxy, n-pentyloxy, phenoxy, hydroxy, acetyl-oxy, methylthio, ethylthio, isopropylthio, thio-(mercapto-), acetylthio, fluoro, chloro, bromo and iodo.

Representative examples of N,N-dialkylanilines useful in the present invention are 4-cyano-N,N-dimethylaniline, 4-acetyl-N,N-dimethylaniline, 4-bromo-N,N-dimethylaniline, ethyl 4-(N,N-dimethylamino) benzoate, 3-chloro-N,N-dimethylaniline, 4-chloro-N,N-dimethylaniline, 3-ethoxy-N,N-dimethylaniline, 4-fluoro-N,N-dimethylaniline, 4-methyl-N,N-dimethylaniline, 4-ethoxy-N,N-dimethylaniline, N,N-dimethylthioaniline, 4-amino-N,N-dimethylaniline, 3-hydroxy-N,N-dimethylaniline, N,N,N',N'-tetramethyl-1,4-dianiline, 4-acetamido-N,N-dimethylaniline, etc.

Preferred N,N-dialkylanilines are substituted with an alkyl group in the ortho-position and include 2,6-diisopropyl-N,N-dimethylaniline, 2,6-diethyl-N,N-dimethylaniline, N,N,2,4,6-pentamethylaniline (PMA) and p-t-butyl-N,N-dimethylaniline.

The autoxidizers are preferably used in the present invention in concentrations of about 4-50% by weight.

The photohardenable compositions of the present invention can be coated upon a support in a conventional manner and used as a photoresist or in photolithography to form a polymer image, or they can be encapsulated as described in U.S. Patents 4,399,209 and 4,440,846 and used to control the release of an image-forming agent. The latter processes typically involve image-wise exposing the photosensitive material to actinic radiation and subjecting the layer of microcapsules to a uniform rupturing force such as pressure, abrasion, or ultrasonic energy whereupon the image-forming agent is released from the microcapsules for reaction with a developer.

Several processes can be used to form color images as explained in U.S. Application Serial No. 339,917. If the microcapsules contain photosensitive compositions which are sensitive to red, green and blue light, images can be formed by direct transmission or reflection imaging or by image processing. Image processing may involve forming color separations (color-seps) corresponding to the red, green and blue component images and sequentially exposing the photosensitive material to three distinct bands of radiation hereinafter designated  $\lambda-1$ ,  $\lambda-2$ , and  $\lambda-3$  through each color separation. Otherwise, it may involve electronic processing in which the image or subject to be recorded is viewed through a Dunn or matrix camera and the output from the camera electronically drives three exposure sources corresponding to  $\lambda-1$ ,  $\lambda-2$ , and  $\lambda-3$ . Alternatively the image may be produced synthetically, e.g., a computer-generated image.

While the discussion herein relates to forming 3-color full color images, 4-color images are also possible. For example, microcapsules containing cyan, magenta, yellow, and black image-forming agents can be provided which have distinct sensitivities at four wavelengths, e.g.,  $\lambda-1$ ,  $\lambda-2$ ,  $\lambda-3$ , and  $\lambda-4$ .

In accordance with the invention, at least one set of the microcapsules in a full color system contains an ionic dye compound. The other sets also may contain an ionic dye compound, or they may contain a different type of photoinitiator.

In accordance with the preferred embodiments of the invention, a full color imaging system is provided in which the microcapsules are sensitive to red, green, and blue light respectively. The photosensitive composition in at least one and possibly all three microcapsules are sensitized by an ionic dye compound. For optimum color balance, the microcapsules are sensitive ( $\lambda_{max}$ ) at about 450 nm, 550 nm and 650 nm respectively. Such a system is useful with visible light sources in direct transmission or reflection imaging. Such a material is useful in making contact prints or projected prints of color photographic slides. They are also useful in electronic imaging using lasers or pencil light sources of appropriate wavelengths.

Because the ionic dye compounds absorb at wavelengths greater than 400 nm, they are coloured. Typically the unexposed dye compound is present with the image-forming in the image areas and, thus, the color of the compound must be considered in determining the color of the image. However, the compound is used in very small amounts compared to the image-forming agent and exposure sometimes bleaches the compound.

The photohardenable compositions of the present invention can be encapsulated in various wall formers

using techniques known in the area of carbonless paper including coacervation, interfacial polymerization, polymerization of one or more monomers in an oil, as well as various melting, dispersing, and coating methods. To achieve maximum sensitivities, it is important that an encapsulation technique be used which provides high quality capsules which are responsive to changes in the internal phase viscosity in terms of their ability to rupture. Because the borate tends to be acid sensitive, encapsulation procedures conducted at higher pH (e.g., greater than about 6) are preferred.

Oil soluble materials have been encapsulated in hydrophilic wall-forming materials such as gelatin-type materials (see U.S. Patent Nos. 2,730,456 and 2,800,457 to Green et al) including gum arabic, polyvinyl alcohol, carboxy-methylcellulose; resorcinol-formaldehyde wall formers (see U.S. Patent No. 3,755,190 to Hart, et al); isocyanate wall-formers (see U.S. Patent No. 3,914,511 to Vassiliades); isocyanate-polyol wall-formers (see U.S. Patent No. 3,796,669 to Kirintani et al); urea-formaldehyde wall-formers, particularly urea-resorcinol-formaldehyde in which oleophilicity is enhanced by the addition of resorcinol (see U.S. Patent Nos. 4,001,140, 4,087,376 and 4,089,802 to Fors et al); and melamine-formaldehyde resin and hydroxypropyl cellulose (see commonly assigned U.S. Patent No. 4,025,455 to Shackleton).

Urea-resorcinol-formaldehyde and melamine-formaldehyde capsules with low oxygen permeability are preferred. In some cases to reduce oxygen permeability it is desirable to form a double walled capsule by conducting encapsulation in two stages.

A capsule size should be selected which minimizes light attenuation. The mean diameter of the capsules used in this invention typically ranges from approximately 1 to 25 microns. As a general rule, image resolution improves as the capsule size decreases. If the capsules become too small, they may become inaccessible in the pores or the fiber of the substrate. These very small capsules may therefore be screened from exposure by the substrate. They may also fail to rupture when exposed to pressure or other rupturing means. In view of these problems, it has been determined that a preferred mean capsule diameter range is from approximately 10 microns. Technically, however, the capsules can range in size up to the point where they become visible to the human eye.

An open phase system may also be used in accordance with the invention instead of an encapsulated one. This can be done by dispersing what would otherwise be the capsule contents throughout the coating on the substrate as discrete droplets. Suitable coatings for this embodiment include polymer binders whose viscosity has been adjusted to match the dispersion required in the coating. Suitable binders are gelatin, polyvinyl alcohol, polyacrylamide, and acrylic lattices. Whenever reference is made to "capsules" and "encapsulation" without reference to a discrete capsule wall in this specification or the appended claims, those terms are intended to include the alternative of an open phase system.

The photosensitive material of the present invention can be used to control the interaction of various image-forming agents.

In one embodiment of the present invention the capsules may contain a benign visible dye in the internal phase in which case images are formed by contacting the exposed imaging material under pressure with a plain paper or a paper treated to enhance its affinity for the visible dye. A benign dye is a colored dye which does not interfere with the imaging photochemistry, for example, by relaxing the excited state of the initiator or detrimentally absorbing or attenuating the exposure radiation.

In a preferred embodiment of the invention, images are formed through the reaction of a pair of chromogenic materials such as a color precursor and a color developer, either of which may be encapsulated with the photohardenable composition and function as the image forming agent. In general, these materials include colorless electron donating type compounds and are well known in the art. Representative examples of such color formers include substantially colorless compounds having in their partial skeleton a lactone, a actam, a sultone, a spiropyran, an ester or an amido structure such as triarylmethane compounds, bisphenylmethane compounds, xanthene compounds, fluorans, thiazine compounds, spiropyran compounds and the like. Crystal Violet Lactone and Copikem X, IV and XI are often used. The color formers can be used alone or in combination.

The developer materials conventionally employed in carbonless paper technology are also useful in the present invention. Illustrative examples are clay minerals such as acid clay, active clay, attapulgite, etc., organic acids such as tannic acid, gallic acid, propyl gallate, etc.; acid polymers such as phenol-formaldehyde resins, phenol acetylene condensation resins, condensates between an organic carboxylic acid having at least one hydroxy group and formaldehyde, etc.; metal salts or aromatic carboxylic acids such as zinc salicylate, tin salicylate, zinc 2-hydroxy naphthoate, zinc 3,5 di-tert butyl salicylate, zinc 3,5-di-( $\alpha$ -methylbenzyl)salicylate, oil soluble metal salts or phenol-formaldehyde novolak resins (e.g., see U.S. Patent Nos. 3,672,935; 3,732,120 and 3,737,410) such as zinc modified oil soluble phenol-formaldehyde resin as disclosed in U.S. Patent No. 3,732,123, zinc carbonate etc. and mixtures thereof.

As indicated in U.S. Patents 4,399,209 and 4,440,846, the developer may be present on the photo-sensitive sheet (providing a so-called self-contained system) or on a separate developer sheet.

In self-contained systems, the developer may be provided in a single layer underlying the microcapsules as disclosed in U.S. Patent No. 4,440,846. Alternatively, the color former and the color developer may be individually encapsulated in photosensitive capsules and upon exposure both capsule sets image-wise rupture releasing color former and developer which mix to form the image. Alternatively, the developer can be encapsulated in non-photosensitive capsules such that upon processing all developer capsules rupture and release developer but the color former containing capsules rupture in only the unexposed or under-exposed

area which are the only areas where the color former and developer mix. Still another alternative is to encapsulate the developer in photosensitive capsules and the color former in non-photosensitive capsules.

The present invention is not necessarily limited to embodiments where the image-forming agent is present in the internal phase. Rather, this agent may be present in the capsule wall of a discrete capsule or in the binder of an open phase system or in a binder or coating used in combination with discrete capsules or an open phase system designed such that the image-wise ruptured capsules release a solvent for the image-forming agent. Embodiments are also envisioned in which a dye or chromogenic material is fixed in a capsule wall or binder and is released by interaction with the internal phase upon rupturing the capsules.

The most common substrate for this invention is a transparent film since it assist in obtaining uniform development characteristics, however, paper may also be used. The paper may be a commercial impact raw stock, or special grade paper such as cast-coated paper or chrome-rolled paper. Transparent films such as polyethylene terephthalate can be used. Translucent substrates can also be used in this invention.

Synthesis Examples 1 and 2 respectively illustrate the preparation of borates and dye-borate compounds.

#### SYNTHESIS EXAMPLE 1

Dissolve triphenylborane in 150 ml dry benzene (1M) under nitrogen atmosphere. Place flask in a cool water bath and, while stirring, add n-BuLi, (1.1 eq.) via syringe. A white precipitate soon formed after addition was started. Stirring is continued about 45-60 min. Dilute with 100 ml hexane and filter, washing with hexane. This resultant Li salt is slightly air unstable. Dissolve the white powder in about 200 ml distilled water and, with vigorous stirring, add aqueous solution of tetramethyl ammonium chloride (1.2 eq. of theoretical in 200 ml). A thick white precipitate forms. Stir this aqueous mixture about 30 min. at room temperature, then filter. Wash collected white solid with distilled water.

As an alternative synthesis, to a 1.0M solution of 2.0 equivalents of 1-butene in dry, oxygen-free dichloromethane, under inert atmosphere, was added slowly dropwise with stirring, 1.0 equivalents of a 1.0M solution of dibromomethane-methylsulfide complex in dichloromethane. The reaction mixture stirred at reflux for 36 hours and the dichloromethane and excess 1-butene were removed by simple distillation. Vacuum distillation of the residue afforded 0.95 equivalents of a colorless mobile oil (Bp 66-7 0.35 mm Hg, <sup>1</sup>BNMR.bs (4.83PPM). Under inert atmosphere, this oil was dissolved in dry, oxygen-free tetrahydrofuran to give a 1.0M solution and 3.0 equivalents of a 2.0M solution of phenylmagnesium chloride in tetrahydrofuran were added dropwise with stirring. After stirring 16 hours, the resultant solution was added slowly with vigorous stirring to 2 equivalents of tetramethylammonium chloride, as a 0.2 M solution, in water. The resulting white flocculate solid was filtered and dried to afford a near quantitative amount of the desired product Mp 250-2°C, <sup>1</sup>BNMR.bs (-3.70PPM).

#### SYNTHESIS EXAMPLE 2

Sonicate a suspension of a borate salt (1 g/10 ml) in MeOH, to make a very fine suspension. Protect flask from light by wrapping with aluminum foil then add 1 equivalent of dye. Stir this solution with low heat on a hot plate for about 30 min. Let cool to room temperature then dilute with 5-10 volumes of ice water. Filter the resultant solid and wash with water until washings are colorless. Suction filter to dryness. Completely dry initiator compound by low heat (about 50°C) in a vacuum drying oven. Initiator is usually formed quantitatively. Analysis by H-NMR indicates 1:1 compound formation typically greater than 90%.

The present invention is illustrated in more detail by the following non-limiting Examples.

#### Example 1

##### Capsule Preparation

1. Into a 600 ml stainless steel beaker, 104 g water and 24.8 g isobutylene maleic anhydride copolymer (18%) are weighed.
2. The beaker is clamped in place on a hot plate under an overhead mixer. A six-bladed, 45° pitch, turbine impeller is used on the mixer.
3. After thoroughly mixing, 3.1 g pectin (polygalacturonic acid methyl ester) is slowly sifted into the beaker. This mixture is stirred for 20 minutes.
4. The pH is adjusted to 4.0 using a 20% solution of H<sub>2</sub>SO<sub>4</sub>, and 0.1 g Quadrol (2-hydroxypropyl ethylenediamine with propylene oxide from BASF) is added.
5. The mixer is turned up to 3000 rpm and the internal phase is added over a period of 10-15 seconds. Emulsification is continued for 10 minutes.
6. At the start of emulsification, the hot plate is turned up so heating continues during emulsification.
7. After 10 minutes, the mixing speed is reduced to 2000 rpm and 14.1 g urea solution (50% w/w), 3.2 g resorcinol in 5 g water, 21.4 g formaldehyde (37%), and 0.6 g ammonium sulfate in 10 ml water are added at two-minute intervals.
8. The beaker is covered with foil and a heat gun is used to help bring the temperature of the preparation to 65°C. When 65°C is reached, the hot plate is adjusted to maintain this temperature for a two or three hour cure time during which the capsule walls are formed.
9. After curing, the heat is turned off and the pH is adjusted to 9.0 using a 20% NaOH solution.
10. Dry sodium bisulfite (2.8 g) is added and the capsule preparation is cooled to room temperature.

Three batches of microcapsules were prepared for use in a full color imaging sheet using the three internal

phase compositions set forth below. Internal Phase A provides a yellow image-forming agent and is sensitive at 420 nm. Phase B provides a magenta image-forming agent and is sensitive at 480 nm, and Phase C contains a cyan image-forming agent and a cationic dye-borate anion complex which is sensitive at 570 nm. The three batches of microcapsules were mixed, coated on a support, and dried to provide a full color imaging sheet.

Internal Phase A (420 nm)

TMPTA 35 g  
 DPHPA 15 g  
 3-Thenoyl-7-diethylamino coumann 15 g  
 2-Mercaptobenzoxazole (MBO) 2.0 g  
 Pentamethylaniline (PMA) 1.0 g  
 Reakt Yellow (BASF) 5.0 g  
 SF-50 (Union Carbide Isocyanate) 1.67 g  
 N-100(Desmodur Polyisocyanate Resin) 3.33 g

Internal Phase B (480 nm)

TMPTA 35 g  
 DPHPA 15 g  
 9-(4'-Isopropylcinnamoyl)-1,2,4-tetrahydro-3H, 6H, 10H[1]-benzopyrano[9, 9A, 1-y]quinolazine-10-one 0.15 g  
 MBO 1.0 g  
 PMA 2.0 g  
 Magenta Color Former (HD-5100 Hilton Davis Chemical Co) 8.0 g  
 SF-50 1.67 g  
 N-100 3.33 g

Internal Phase C (570 nm)

TMPTA 50 g  
 Cationic Dye Compound No. 2 0.15 g  
 PMA 2.0 g  
 Cyan Color Former (S-29663 Hilton Davis Chemical Co.) 4.0 g  
 SF-50 1.67 g  
 N-100 3.33 g

Example 2

Capsule Preparation

1. Into a 600 ml stainless steel beaker, 110 g water and 4.6 g isobutylene maleic anhydride copolymer (dry) are weighed.
  2. The beaker is clamped in place on a hot plate under an overhead mixer. A six-bladed, 45° pitch, turbine impeller is used on the mixer.
  3. After thoroughly mixing, 4.0 g pectin (polygalacturonic acid methyl ester) is slowly sifted into the beaker. This mixture is stirred for 2 hours at room temperature (800-1200 rpm).
  4. The pH is adjusted to 7.0 with 20% sulfuric acid.
  5. The mixer is turned up to 3000 rpm and the internal phase is added over a period of 10-15 seconds. Emulsification is continued for 10 minutes. Magenta and yellow precursor phases are emulsified at 25-30° C. Cyan phase is emulsified at 45-50° C (oil), 25-30° C (water).
  6. At the start of emulsification, the hot plate is turned up so heating continues during emulsification.
  7. After 10 minutes, the pH is adjusted to 8.25 with 20% sodium carbonate, the mixing speed is reduced to 2000 rpm, and a solution of melamine-formaldehyde prepolymer is slowly added which is prepared by dispersing 3.9 g melamine in 44 g water, adding 6.5 g formaldehyde solution (37%) and heating at 60° C until the solution clears plus 30 minutes.
  8. The pH is adjusted to 6.0, the beaker is covered with foil and placed in a water bath to bring the temperature of the preparation to 65° C. When 65° C is reached, the hot plate is adjusted to maintain this temperature for a two hour cure time during which the capsule walls are formed.
  9. After curing, mixing speed is reduced to 600 rpm, formaldehyde scavenger solution (7.7 g urea and 7.0 g water) is added and the solution was cured another 40 minutes.
  10. The pH is adjusted to 9.5 using a 20% NaOH solution and stirred overnight at room temperature.
- Three batches of microcapsules were prepared as above for use in a full color imaging sheet using the three internal phase compositions set forth below.

Yellow Forming Capsules (420 nm)

TMPTA 35 g  
 DPHPA 15 g  
 3-Thenoyl-7-diethylamino coumann 15 g  
 2-Mercaptobenzoxazole (MBO) 2.0 g

2,6-Diisopropylaniline 10 g  
 Reakt Yellow (BASF) 50 g  
 N-100(Desmodur Polysocyanate Resin) 333 g

Magenta Forming Capsules (550 nm)  
 TMPTA 50 g

Compound 8A 0.2 g

2,6-Diisopropylaniline 2.0 g

HD5100 (Magenta color precursor from Hilton-Davis Chemical Co.) 12.0 g

Cyan Forming Capsules (650 nm)  
 TMPTA 50 g

Compound 11 H 0.31 g

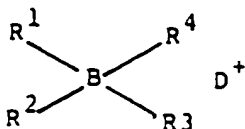
2,6-diisopropylaniline 2.0 g

Cyan Precursor (CP-177 of Hilton-Davis Chemical Co.) 6 g

The three batches of microcapsules were blended together and coated on a support to provide an imaging material in accordance with the present invention.

## Claims

1. A photohardenable composition comprising a free radical addition polymerizable or crosslinkable compound and an ionic dye-counter ion compound, said ionic dye-counter ion compound being capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization or crosslinking of said polymerizable or crosslinkable compound.
2. A photohardenable composition according to claim 1 wherein prior to exposure, said ionic dye-counter ion compound is a stable, non-transient compound.
3. A photohardenable composition according to claim 1 or claim 2 wherein said ionic dye-counter ion compound is soluble in said free radical addition polymerizable or crosslinked compound.
4. A photohardenable composition according to any preceding claim wherein said ionic dye-counter ion compound is characterized in that following exposure of said compound to light, said dye is excited to a singlet state which is quenched by said counter ion.
5. A photohardenable composition according to claim 4, wherein following exposure of said ionic dye-counter ion compound to light, an electron is transferred from said dye to said counter ion or from said counter ion to said dye and the rate of said electron transfer is greater than a diffusion controlled rate.
6. A photohardenable composition according to any preceding claim, wherein said polymerizable or crosslinkable compound is an ethylenically unsaturated compound.
7. A photohardenable composition according to any preceding claim, wherein said compound is an anionic dye compound.
8. A photohardenable composition according to claim 7, wherein said ionic dye counter ion compound is an anionic dye-iodonium ion complex or an anionic dye-pyrylium ion complex.
9. A photohardenable composition of claim 7 or claim 8, wherein said dye is a xanthene dye or an oxonol dye.
10. A photohardenable composition according to any one of claims 1 to 6, wherein said ionic dye counter ion compound is a cationic dye-borate anion compound.
11. The photohardenable composition of claim 10, wherein said cationic dye-borate anion compound is represented by the formula (I):



where  $D^+$  is a cationic dye moiety and  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently selected from alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic and saturated or unsaturated heterocyclic groups.

12. A photohardenable composition according to claim 11, wherein said cationic dye is a cationic methine, polymethine, triarylmethane, indoline, azine, thiazine, xanthene, oxazine, or acridine dye.

13. A photohardenable composition according to claim 12, wherein said cationic dye is a cationic cyanine, carbocyanine, hemicyanine, rhodamine, or azamethine dye.

14. A photohardenable composition according to any one of claims 11 to 13, wherein at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is an alkyl group and at least one is an aryl group.

15. A photosensitive material comprising a support having on a surface thereof a layer of a photohardenable composition according to any preceding claim.

16. A photosensitive material comprising a support having a layer of microcapsules on one surface thereof, said microcapsules having an image-forming agent associated therewith and containing an internal phase including a photohardenable composition according to any one of claims 1 to 14.

17. A photosensitive material according to claim 16, wherein said image-forming agent is a substantially colourless chromogenic material.

18. A photosensitive material according to claim 16 or claim 17, which is useful in forming full color images and wherein said microcapsules include a first set of microcapsules having a cyan image-forming agent associated therewith, a second set of microcapsules having a magenta image-forming agent associated therewith and a third set of microcapsules having a yellow image forming agent associated therewith, at least one of said first, second and third sets of microcapsules containing said photohardenable composition contain said ionic dye-counter ion compound.

19. A photosensitive material according to claim 18, which is useful in forming images by a process which comprises the steps of image-wise exposing said microcapsules to three distinct wavelengths of actinic radiation which respectively harden said first, second and third sets of microcapsules and subjecting said microcapsules to a uniform rupturing force.

20. A photosensitive material according to claim 19, wherein at least one of said wavelengths is greater than 400 nm.

21. A photosensitive material according to claim 20, wherein said three distinct wavelengths are red, green and blue light.



European Patent  
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## EUROPEAN SEARCH REPORT

Application number

EP 86 30 8967

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	JP-A-80 039 162 (GENERAL ELECTRIC CO.) * Abstract *	1-15	C 08 F 2/50 G 03 C 1/68
A	US-A-3 775 130 (T. ENOMOTO et al.) * Claim 1 *	1-15	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 F G 03 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-02-1987	Examiner CAUWENBERG C. L. M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if considered with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	